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54 Crosslinked acetoacetic ester polymers.

57 Cross-linked polymers are obtained by transesterifying an alkyl monofunctional acetoacetate with a polyhydroxy functional monomer or polymer so as to produce a polyacetoacetic functional monomer or polymer and reacting said polyacetoacetic functional monomer or polymer with a poly α , β -unsaturated ester in the presence of a strong base catalyst or in the presence of an organometallic catalyst. The poly α , β -unsaturated ester is formed by reacting crotonic, acrylic, methacrylic, maleic, cinnamic or itaconic acids with polyhydroxy or epoxy functional monomers and polymers.

Descripti n

CROSSLINKED ACETOACETIC ESTER POLYMERS

The present invention relates to crosslinked polymers and processes for the manufacture thereof. More particularly, the present invention relates to a cross-linked polymer system resulting from the reaction of acetoacetate esters and α,β -unsaturated esters:

Several disadvantages have been experienced with current ambient and thermosetting compositions and especially those formulated with melamine or urea-formaldehyde resins since during the curing cycle toxic volatiles, including free formaldehyde evolve. These compositions are generally cured at elevated temperatures, i.e. at about 275° F (135° C) or higher. It has also been observed that while the use of isocyanates offers excellent cure at lower temperatures, i.e. from ambient temperature to about 250° F (120° C), nonetheless isocyanates are very toxic and compositions containing them, when cured at ambient or room temperature, produce undesirable side reactions, especially if moisture is present. Epoxy resin containing compositions can cure over a wide temperature range depending upon the type of curing agent employed. However, curing agents for epoxy resins are often very toxic and act as sensitizers to humans. Moreover, their exterior durability is unsatisfactory, limiting their use generally to primer applications.

The present invention relates to a process for producing a cross-linked polymer. The process comprises transesterifying an alkyl acetoacetate with a polyhydroxy functional monomer or polymer in the presence or not of a catalyst and reacting the thus formed acetoacetic functional monomer or polymer with a polyfunctional α,β -unsaturated ester in the presence of a strong base catalyst or an organometallic catalyst. The present invention also relates to the cross-linked polymers produced by this process.

It has now been found that the disadvantages associated with other crosslinking systems can be avoided by the practice of the present invention which provides a crosslinking composition which is curable not only without the production of any toxic by-products and also at low temperatures, i.e. ambient temperature to about 350° F (175° C) without adverse side reactions. At elevated temperatures, satisfactory cures can be obtained in the shortest time. An advantageous elevated curing temperature range is from about 180° F to 300° F (80° - 150° C). The quality of coatings produced using the crosslinked compositions of the present invention is similar to that of current coatings in primer application or high durability top coats. The crosslinked compositions of the present invention, when used as a coating composition, also can offer the advantage of being compliance coatings which meet the current United States Environmental Protection Agency's (EPA) VOC (volatile organic compound) regulations. Coatings or films produced using the crosslinked compositions of the present invention exhibit excellent adhesion, excellent solvent resistance, excellent gloss retention, good flexibility and excellent hardness. These properties are achieved when the polymer system is coated over numerous substrates such as chromate treated aluminum, zinc and iron phosphate treated steel and various plastics such as polyamides, polycarbonates, ABS, and polyphenylene oxide.

Polymers prepared from the composition of the present invention are useful as coatings for farm implements, automotive top coats, primers, aluminum extrusions, office furnishings and wood products. Industries having a use for such coatings have been in need of a high quality, non-toxic, low temperature cure coating meeting the EPA's VOC regulations. The present invention fulfills such a need.

The present invention provides both a method for preparing the acetoacetate ester and poly α,β -unsaturated ester components for a polymer as well as the crosslinked polymer itself.

The process for producing the crosslinked polymer comprises transesterifying an alkyl monofunctional acetoacetate with a polyhydroxy functional monomer or polyhydroxy functional polymer in the presence or not of a catalyst so as to produce a polyacetoacetic functional monomer or a polyacetoacetic functional polymer and, subsequently, reacting the thus formed acetoacetic functional monomer or polymer with an α,β -unsaturated material in the presence of a strong base catalyst or, in accordance with another embodiment of the present invention, in the the presence of an organo metallic catalyst.

Films produced in accordance with the present invention exhibit good hardness, excellent solvent resistance, excellent adhesion, excellent flexibility, and excellent gloss retention after accelerated exposure. Advantageously, coatings using the present novel systems can be formulated with very low volatile organic contents as to comply with EPA regulations.

In one embodiment of the present process, one reaction involved is known as the Michael Reaction. The Michael Reaction is described in Mechanism and Structure in Organic Chemistry, (E.S. Gould, p. 392-394; Holdt Rinehard and Winston, New York, 1959.) In general, in the Michael Reaction an acetoacetic ester material forms a carbanion in the presence of a strong base. The carbanion then reacts with the α,β -unsaturated carbonyl compound.

In the present process, the reaction can be conducted with stoichiometric amounts, or a slight excess, of the polyacetoacetic functional compounds relative to the poly α,β -unsaturated materials. Advantageously, and thus preferably, an excess of the acetoacetic functional compound(s) is (are) used so as to ensure a complete reaction with the poly α,β -unsaturated material. The stoichiometric excess ensures a complete reaction which prevents a coating produced from the present composition from having undesired yellowing and decreased exterior coating durability. The ratio of the polyacetoacetic functional compound(s) to the poly α,β -unsaturated crosslinking compound(s) is from 0.50 - 1.50 to 1.5 - 0.50 and more advantageously is from about 1.0:1.0 to about 1.0:0.8.

alkyd. The ethanol was removed through the Barrett receiver. The procedure was the same as in Example I. The resulting modified alkyd has a Y-Z viscosity at 60% nonvolatiles and an equivalent weight of 846 on a solids basis.

Example VII

An acetoacetic functional acrylic was prepared by first preparing a hydroxy functional acrylic. This was performed by reacting 172 grams of styrene, 542 grams of butyl methacrylate, 343 grams of butyl acrylate, 570 grams of hydroxyethyl acrylate and 116 grams of cumene hydroperoxide in refluxing methyl amyl ketone (1,085 grams) and cumene hydroperoxide (28 grams). The monomers and catalyst were added simultaneously and continuously over four hours to the refluxing solvent. The reaction was performed in a five liter reactor equipped with an agitator, and addition funnel, a thermometer, a Barrett distilling receiver and water condenser. After the monomers were added, the resin was held at a reflux temperature of $143 \pm 3^\circ\text{C}$ until a terminal viscosity of D-E was reached.

The resulting acrylic resin was then cooled to 100°C at which point 640 grams of ethyl acetoacetate and 4 grams of paratoluene sulfonic acid were added. The transesterification by-product, ethanol, was removed through the Barrett receiver as described in Example I. The final product has a D-E viscosity at 58% nonvolatiles in methyl amyl ketone and an equivalent weight of 410 on a solids basis.

Examples VIII-XVIII

Examples VIII to XVIII illustrate exemplary pigmented coatings prepared from the acetoacetic functional polymers of Examples I to VII.

Example VIII

A gloss white enamel was formulated with a PVC content of 16% and at a volume solids of 52%.

The acetoacetic functional ester material, prepared according to Example I, was reacted with an acrylate functional acrylic resin as the α,β -unsaturated crosslinker. The copolymer GMA/acrylic acid (AA)/BA/Styrene (S)/MMA-22.1/11.2/22.1/26.8/17.8 weight ratio respectively, 59% nonvolatiles in xylene was reacted at a stoichiometric ratio of 1:1. The reaction was conducted in the presence of tetrabutyl ammonium hydroxide catalyst, 2% level based on vehicle solids content and then baked for 30 minutes at 250°F (120°C) on a substrate composed of treated cold rolled steel. Thereafter, the resulting white enamel was evaluated and had the following properties:

Gloss - 94/60°, 60/20°.

Pencil Hardness - 2H.

Solvent Resistance - 100+ MEK double rubs and

Crosshatch Adhesion -taped 100% retention.

Example IX

A gloss white enamel was formulated with a PVC content of 16% by a volume solids of 52%. This system can be tinted with a commercial tinting system.

The acetoacetic functional ester material, prepared according to Example II, was reacted with, as the α,β -unsaturated crosslinker, the acrylate functional acrylic resin of Example VII at a stoichiometric ratio of 1:1. The reaction was conducted in the presence of tetrabutyl ammonium hydroxide catalyst, 2% based on a vehicle solids content. The gloss white enamel was baked for 30 minutes at 250°F (120°C) on a treated cold rolled steel substrate. After baking, the enamel was evaluated and exhibited the following properties:

Gloss - 98/60°, 77/20°.

Pencil Hardness - H-2H.

Solvent Resistance - 100+ MEK double rubs, and

Crosshatch Adhesion - taped 100% retention.

A second portion of the above gloss white enamel was baked for 60 minutes at 180°F (80°C) on treated cold rolled steel substrate. After baking, the white enamel was evaluated and exhibited the following properties:

Gloss - 94/60°, 82/20°.

Pencil Hardness - H.

Solvent Resistance - 50 MEK double rubs and

Crosshatch Adhesion -taped 100% retention.

Example X

A conductive dark gray epoxy ester primer for metal and plastic was prepared as follows. This coating was formulated with an active PVC of 21.87% (conductive carbon black and titanium dioxide) and a total PVC of 42.9%.

The acetoacetic ester, prepared in accordance with Example IV, was reacted with, as the α,β -unsaturated crosslinker, trimethylolpropane triacrylate at a stoichiometric ratio of 1:1, in the presence of a tetrabutyl ammonium hydroxide catalyst, at a 2% level based on vehicle solids content.

Thereafter, a portion of the primer was baked for 30 minutes at 250°F (120°C) on treated cold rolled steel, nylon and polycarbonate.

The resulting primer exhibited the following characteristics:

Pencil Hardness - B+ initially, H in 72 hours, and

Solvent Resistance - 35 MEK double rubs initially, 50+ in 72 hours.

A second portion of the primer was baked for 22 minutes at 340°F (170°C) on treated cold rolled steel.

The resulting primer exhibited the following properties:

- 5 Pencil Hardness - H initially, 2H in 72 hours, and
Solvent Resistance - 60 MEK double rubs initially, 100+ in 72 hours.

Example XI

- 10 A polyester gloss white enamel was formulated with a PVC content of 18% at a volume solids of 40%.
The acetoacetic ester, prepared in accordance with Example V, was reacted with, as the α,β -unsaturated crosslinker, trimethylolpropane triacrylate, at two different stoichiometric ratios. The two reaction products were cured to prepare two different polyester gloss white enamels. Each polyester gloss white enamel was thereafter baked and evaluated as follows.

- 15 (a) The first crosslinked polymer was prepared at an acetoacetic ester: acrylate functional crosslinker stoichiometric ratio of 1:0.80 in the presence of a tetrabutyl ammonium hydroxide catalyst, 2% on vehicle solids. The enamel prepared from the polymer was baked for 30 minutes at 250°F (120°C) on treated cold rolled steel and exhibited the following properties

Gloss - 95/60°, 85/20°,

Pencil Hardness - F-H,

- 20 Solvent Resistance - 50 MEK double rubs and

Crosshatch Adhesion - taped 100% retention.

- (b) The second crosslinked polymer was prepared at an acetoacetic ester: acrylate functional crosslinker stoichiometric ratio of 1:0.60 in the presence of a tetrabutyl ammonium hydroxide catalyst, 2% of vehicle solids. The enamel prepared from the crosslinked polymer was baked for 30 minutes at 250°F (120°C) on treated cold rolled steel. The baked enamel had the following properties:

25 Gloss - 92/60°, 74/20°,

Pencil Hardness - H,

Solvent Resistance - 50 MEK double rubs and

Crosshatch Adhesion - taped 100% retention.

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Example XII

A gloss white enamel was formulated with a PVC content of 16% and a volume solids of 44%.

- 35 The acetoacetic ester, prepared in accordance with Example III, was reacted with, as the α,β -unsaturated crosslinker, trimethylolpropane triacrylate, at a stoichiometric ratio of 1:1 in the presence of a tetrabutyl ammonium hydroxide catalyst at a 2% level of vehicle solids content. The thus prepared crosslinked polymer was air dry cured for 96 hours on treated cold rolled steel.

The resulting enamel was evaluated and exhibited the following characteristics:

Gloss - 92/60°, 74/20°,

Pencil Hardness - 2H,

- 40 Solvent Resistance - 50 MEK double rubs 68 hours, 100 MEK double rubs 96 hours, and

Crosshatch Adhesion - taped 100% retention.

Example XIII

- 45 A gloss white acrylic enamel was formulated with a PVC content of 20% at a volume solids of 45.5%.

- The acetoacetic ester, prepared in accordance with Example II, was reacted with, as the α,β -unsaturated crosslinker, crotonate functional acrylic resin, at a stoichiometric ratio of 1:0.80 in the presence of tetrabutyl ammonium hydroxide at 2% level on vehicle solids content. The crosslinker may be further identified as GMA/BA/S/MMA/crotonic acid with weight ratios, respectively, of 21.7/21.7/26.0/17.4/13.2 at 60% nonvolatiles in xylene. The thus prepared crosslinked polymer was baked for 30 minutes at 250°F (120°C) on cold rolled steel.

- 50 The resulting enamel was evaluated and exhibited the following properties:

Gloss - 88/60°, 62/20°,

Pencil Hardness - F-H,

- 55 Solvent Resistance - 50 MEK double rubs and

Crosshatch Adhesion - taped 100% retention.

Example XIV

- 60 A gloss white acrylic enamel was formulated with a PVC content of 20% at a volume solids of 45.5%.

- The acetoacetic ester, prepared in accordance with Example VII, was reacted with, as the α,β -unsaturated crosslinker, the crotonate functional acrylic of Example XIII, at a stoichiometric ratio of 1:0.80 in the presence of a tetrabutyl ammonium hydroxide catalyst, 5% of vehicle solids. The resulting crosslinked polymer was baked for 30 minutes at 250°F (120°C) on treated cold rolled steel. The resulting enamel was evaluated and exhibited the following properties:

Gloss - 94/60°, 86/20°,

- 65 Pencil Hardness - H

TABLE I

5	(1) trimethylolpropane triacrylate	gelled
	(2) trimethylolpropane trimethacrylate	gelled
	(3) Maleic modified polyester (a)	gelled
10	(4) itaconate modified polyester (b)	gelled
	(5) crotonic acid modified acrylic (c)	gelled
15	(6) trimethylolpropane tricinamate	gelled

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- 20 (a) Maleic anhydride/propylene glycol 1.0/1.1
molar ratio reduced to 60% nonvolatiles in
methyl amyl ketone.
- 25 (b) itaconic acid/propylene glycol 1.0/1.1
molar ratio reduced to 60% nonvolatiles in
methyl amyl ketone.
- 30 (c) GMA/BA/S/MMA/Crotonic acid -
21.7/21.7/26.0/17/4/13.2 weight ratio
respectively - 60% nonvolatiles in xylene.

35 The gellation of these blends indicate that the trimethylol propane triacetoacetate will react and crosslink
with the various forms of α,β -unsaturated ester materials.

40 Examples XX-XXIII illustrate exemplary coatings prepared from the acetoacetic functional polymers of
Examples I to VII in the presence of an organometallic catalyst.

Example XX

45 A stock mixture of hexanediol diacetoacetate from Example II and an acrylate functional acrylic resin was
prepared. The acrylate functional acrylic resin was prepared by reacting acrylic acid on to a glycidyl
methacrylate functional acrylic containing a 25/25/30/20 weight ratio of glycidyl methacrylate/butyl
acrylate/styrene/methylacrylate respectively. The acrylate equivalent weight base on 100% nonvolatile is 640.
The stoichiometric ratio of the reactants is 1.0:1.0 on solids. Films of each mixture were prepared on cold
rolled steel and baked for 15 to 30 minutes at 250°F and 300°F (120°C and 150°C). The resulting films had the
properties set forth in the following table.

50 The reverse impact referred to in the table is a measurement of the adhesive quality of the coated system. It
is measured generally by dropping a known weight from a given height onto the side of a substrate (generally
metal) opposite to that which has been coated with the crosslinked polymer. Failure is noted when the coating
covering the resultant dimple in the substrate exhibits a star-like crack. The quantity in which the failure is
measured is the product of the height and weight causing the failure.

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			Solvent		
			Resistance		Reverse
5		Bake	MEK Double	Pencil	Impact
	Catalyst	Schedule *	Rubs	Hardness	In.Lbs (Cm.Kg.)
10	1) Chrome Octoate 0.12% Cr	30'x300°F	20	2B	20 (23)
15	m) Vanadium Octoate 0.08% V	30'x300°F	50	HB	20 (23)
20	n) Manganese (III) Ace- to acetate 0.12% Mn	30'x300°F	50	H	20 (23)
25	o) Cobalt (II) Acetoaceto- nate 0.12% Co	30'x300°F	50	HB	20 (23)
30					

* 250°F = 120°C; 300°F = 150°C

The following example demonstrates the cure and film properties of a gloss black enamel using the coating system in Example VIII and cured with several different metallic carboxylates.

Example XXI

A gloss black enamel coating was formulated with the acetoacetic ester/acrylate functional blend as given in Example VIII. The coating was formulated with an active PVC of 3.8% at a volume solids of 52%. Various metal carboxylates were added to samples of this paint at a level of 0.06% metal based on vehicle solids. The paint was sprayed onto cold rolled steel and baked for fifteen minutes at 250°F (120°C). The test results of these paint systems are given.

50	Catalyst	Solvent	Crosshatch	Gloss 60°/20°	Pencil Hardness	
		Resistance-MEK				Adhesion Taped
		Double	Rubs			
55	a) Control, no catalyst	Solvates	0	87/69	<6B	
	b) Potassium Octoate	50	100%	87/63	F	
	c) Lithium Neodecanoate	50	100%	88/74	HB	
60	d) Cerium Naphthenate	50	100%	87/71	2H	
	e) Manganese Octoate	50	100%	88/79	2H	
	f) Cobalt Naphthenate	50	100%	87/71	H	

		Stability	Cure	Solvent	Pencil	Reverse
		27°C	Schedule *	MEK-DR	Hardness	Impact
						In.Lbs (Cm.Kg.)
5	a) Manganese	15 hr.	15'X300°F	50	H	20
	Octoate					(23)
	0.12% Mn					
10	b) Manganese	40 days	15'X300°F	50	H	20
	Octoate					(23)
	0.12% Mn					
15	0.50% Methyl Ethyl Ketoxime					
20						
	* 300°F = 150°C					

25 Stability is the time from which the example is catalyzed with the organometallic compound to the time it is gelled solid.

30 Claims

- 35 1. A process for preparing a crosslinked polymer characterized in that a polyacetoacetic functional monomer or polymer obtained by transesterifying an alkyl monofunctional acetoacetate with a polyhydroxy functional monomer or a polyhydroxy functional polymer is reacted, in the presence of a strong base catalyst effective to initiate a Michael Reaction or in the presence of an organometallic compound, with a poly a,B-unsaturated ester obtained by reacting a crotonic, acrylic, methacrylic, maleic or itaconic acid with a polyhydroxy or epoxy functional monomer or polymer, or a mixture thereof.
- 40 2. A process as claimed in Claim 1, wherein said strong base is selected from lithium hydroxide, sodium hydroxide, potassium hydroxide, tetramethylammonium hydroxide, tetrabutyl ammonium hydroxide, benzyl trimethyl ammonium hydroxide, dimethyl ethanol amine, ammonia, triethylamine, and mixtures thereof.
- 45 3. A process as claimed in Claim 1, wherein said organometallic compound is a carboxylate selected from (1) the 2-ethyl hexanoates or octoates of lead, cobalt, manganese, zinc, calcium, iron, zirconium, lanthanum, chromium, potassium or vanadium; (2) the naphthenates of lead, cobalt, manganese, zinc, calcium, iron, potassium or cerium; (3) the tallates of lead, cobalt, manganese, calcium or iron; (4) the neodecanoates of calcium, balt, manganese, lead, zinc, zirconium or iron; (5) the isononoates of calcium, cobalt, lead manganese, zinc, zirconium or iron (6) the heptanoates of calcium, cobalt, lead, manganese, zinc, zirconium or iron and mixtures thereof.
- 50 4. A process as claimed in Claim 1, wherein said organometallic compound is selected from acetoacetates of manganese, cobalt, chromium, lead, calcium, cerium, iron, and mixtures thereof.
- 55 5. A process as claimed in any one of Claims 1, 3 and 4, wherein said organometallic compound catalyst is present in an amount sufficient to provide 0.02 to 0.8 percent metal based on total vehicle solids.
- 60 6. A process for preparing a crosslinked polymer comprising reacting an acetoacetic functional monomer or polymer with an a, B-unsaturated ester in the presence of a strong base catalyst effective to initiate a Michael Reaction, said a, B-unsaturated ester being formed by reacting a crotonic, maleic or itaconic acid with a polyhydroxy or epoxy functional monomer or polymer, or a mixture thereof.
- 65 7. A process for preparing a crosslinked polymer comprising reacting trimethylolpropane triacetoacetate with an a, B-unsaturated ester in the presence of a strong base catalyst effective to initiate a Michael Reaction, said a, B-unsaturated ester being formed by reacting acrylic acid with glycidyl methacrylate, butylacrylate, styrene and methyl methacrylate.
8. A process for preparing a crosslinked polymer comprising reacting a polyacetoacetic functional monomer or polymer with a poly a, B-unsaturated ester in the presence of an organometallic compound, said poly a, B-unsaturated ester being the ester of crotonic, acrylic, methacrylic, maleic or itaconic acid with a polyhydroxy or epoxy functional monomer or polymer.
9. A process for preparing a crosslinked polymer comprising reacting a polyacetoacetic functional monomer or polymer with a poly a, B-unsaturated ester in the presence of a metallic compound, said poly